FORMALDEHYDE 2016

$H_2C=O$ MW: 30.03 CAS: 50-00-0 RTECS: LP8925000

METHOD: 2016, Issue 1 **EVALUATION: FULL** **Issue 1: 15 January 1998**

OSHA : 0.75 ppm; 2 ppm STEL
NIOSH: 0.016 ppm; C 0.1 ppm; carcinogen
ACGIH: C 0.3 ppm; suspected human carcinogen
(1 ppm = 1.23 mg/m^3 @ NTP)

PROPERTIES: gas; BP −19.5 °C; vapor density 1.067 (air = 1); explosive range 7 to 73 % (v/v) in air

SYNONYMS: methanal; formalin (aqueous 30 to 60% w/v formaldehyde), methylene oxide

SAMPLING

SAMPLER: CARTRIDGE
(Silica gel containing cartridge coated with 2,4-dinitrophenylhydrazine)

FLOW RATE: 0.1 to 1.5 L/min

VOL-MIN: 1 L @ 0.3 mg/m^3
-MAX: 15 L @ 2.5 mg/m^3

SHIPMENT: Place caps on cartridge. Ship cold.

SAMPLE STABILITY: 14 days @ 4 °C

BLANKS: 2 to 10 field blanks per set
6 to 10 media blanks per set

ACCURACY

RANGE STUDIED: 0.025 to 2.45 mg/m^3 [1]
(22-L sample)

BIAS: + 4.4%

OVERALL PRECISION ($\hat{S}_{rT}$): 0.057 [1]

ACCURACY: ± 19.0%

MEASUREMENT

TECHNIQUE: HPLC, UV DETECTION

ANALYTE: 2,4-dinitrophenylhydrazone derivative of formaldehyde

EXTRACTION: 10 mL carbonyl-free acetonitrile eluted through the cartridge @ 3 mL /min

INJECTION VOLUME: 20 µL

MOBILE PHASE: 45% acetonitrile/55% water (v/v), 1.3 mL/min, isocratic

COLUMN: C_{18}, 150 x 3.9-mm, 5-µm particles (with a C_{18} guard column), Symmetry™ or equivalent

DETECTOR: UV @ 360±2 nm

CALIBRATION: standard solutions of formaldehyde spiked onto samplers

RANGE: 0.31 to 38 µg per sample [1,2]

ESTIMATED LOD: 0.09 µg per sample [1]

PRECISION ($\bar{S}_r$): 0.023 @ 2.2 to 46.4 µg per sample [1]

APPLICABILITY: The working range is 0.021 to 2.5 mg/m^3 for a 15-L air sample. This method can be used for the determination of formaldehyde for both STEL and TWA exposures.[1]

INTERFERENCES: Ozone has been observed to consume the 2,4-DNPH reagent and degrades the hydrazone derivative. Other aldehydes may react with the 2,4-DNPH but can be chromatographically resolved under appropriate conditions.

OTHER METHODS: NIOSH Method 5700 [2] uses a similar analysis procedure. The analysis procedure used in this method has also been used for the determination of formaldehyde in automobile exhaust [3]. Other methods available for formaldehyde analysis include OSHA Method 52 [4], NIOSH methods 3500 [5], and 2541 [6].

REAGENTS:

1. 2,4-Dinitrophenylhydrazine (DNPH), recrystallized from ethanol.
2. Formaldehyde stock solution,* 1 mg/mL (see APPENDIX).
3. DNPH derivative of formaldehyde (MW=210.15) [7]. Derivative is commercially available from Supelco, Inc.
4. Acetonitrile, distilled in glass, low carbonyl content.**
5. Ethanol, absolute, low carbonyl content.**
6. Calibration stock solution. Dissolve 40 mg formaldehyde DNPH derivative and 50 mg DNPH in 100 mL of acetonitrile.
7. Water, deionized and distilled.

* See SPECIAL PRECAUTIONS

** Carbonyl content of the solvents can be determined by mixing the solvent with DNPH-coated sorbent and analyzing by HPLC. Formaldehyde content should be similar to sorbent tube manufacturer's specification.

EQUIPMENT:

1. Sampler: Plastic holder containing 0.35 g of 500-1000 µm silica gel coated with 0.9 mg 2,4-dinitrophenylhydrazine. Pressure drop across the sampler should be less than 20 inches of water (5 kPa) at 1.5 L/min. Samplers are commercially available. (Waters Sep-Pak XPoSure Aldehyde Sampling Cartridge; similar types of samplers are manufactured by Supelco [Supelclean LPD DNPH Cartridge, part no. WAT047205] and SKC [catalog no. 226-119, DNPH coated silica gel tube].)
2. Personal sampling pump, 0.1 to 1.5 L/min, with flexible polyethylene or PTFE tubing.
3. Vials, 4-mL glass.
   NOTE: Do NOT use vials with 'polycone' liners (source of high formaldehyde blank).
4. Liquid chromatograph with UV detector, recorder, integrator, and column (page 2016-1).
5. Syringes, 10-, 25-, 50-, 100- and 1000-µL.
6. Volumetric flasks, 10-, 100-mL and 1-L.
7. Pipets, 0.1-, 0.5-, 1.0-, and 3-mL glass, delivery, with pipet bulb.
8. Graduated cylinders, glass, 25-mL.
9. Equipment for standardizing formaldehyde stock solution, Burets, 50-mL.
10. pH meter.
11. Magnetic stirrer.
12. Beaker, 50-mL.
13. Disposable syringes, 10-mL.
14. Disposable syringe filters

SPECIAL PRECAUTIONS: Formaldehyde is a suspect carcinogen [9] and should be handled in a hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Open sampler packet and remove end caps.
3. Attach sampler to the sampling pump with flexible tubing. Sampler is bi-directional (Waters and Supelco) and can be connected at either end.
   NOTE 1: The sampler has no backup section to detect breakthrough. If high concentrations are anticipated, connect two samplers in series. The back pressure of the sampling train will be increased and flow rate limited.
   NOTE 2: The glass tube can be sampled in one direction with the larger bed in the front. These samplers have a backup section, and should not be used in tandem.
4. Sample 1 to 15 L of air at 0.1 to 1.5 L/min flow rate.
5. Replace end caps on the sampler and return sampler to packet with appropriate sampling information included. Keep samples away from heat (e.g., storage in automobile, etc.)
6. Ship samples on ice, if possible. Samples are stable at room temperature for 4 days before significant analyte losses are observed.

SAMPLE PREPARATION:

NOTE: Check acetonitrile for formaldehyde content by eluting a blank cartridge. The formaldehyde levels should be below the limit of detection. Since background formaldehyde levels on the samplers may change during storage and/or the acetonitrile may become contaminated, always compare samples to a sampler blank from the same lot, stored under the same conditions.

7. a. Elute the formaldehyde derivative from cartridge samplers with 10 mL of acetonitrile into a 10-mL volumetric flask. Control rate of elution to <3 mL/min. Higher flow rates may result in reduced recovery of formaldehyde. Add acetonitrile to the flask to make the total volume 10 mL.
   b. For the glass sorbent tube, place front and back sorbent sections into separate 4-mL vials, add 3 mL of acetonitrile to each vial, and allow to stand for 30 to 60 min with frequent agitation.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working standards over the range of interest.
   a. Pipet aliquots of calibration stock solution (e.g., 10, 50, 100, 300, and 1000 µL) into 10-mL volumetric flasks.
   b. Bring the volume of each working standard to 10 mL acetonitrile.
   b. Transfer a 3-mL aliquot to a 4-mL vial, cap the vial, and analyze (steps 11 through 14).
   c. Prepare a calibration graph, peak area vs. µg formaldehyde.
9. Determine recovery of formaldehyde from sampler.
   a. Add aliquots ($\geq$50 µL) of a calibrated formaldehyde solution to unused samplers to prepare recovery standards. Recovery is expected to be between 95-100%.
      NOTE: If the volume of calibrated formaldehyde solution to be added is less than 50 µL, prepare a 1:10 or 1:100 dilution of the calibrated formaldehyde solution, so the volume added is 50 µL or more. Then draw a small volume (10 mL) of air through the sampler with a disposable 10-mL syringe to pull the solution into the sorbent bed. In cases where the glass sampling tubes are used, the solution volume added should be 10 to 30 µL to prevent flooding the tube.
   b. Desorb the recovery standards in the same manner as the samplers (step 7).
   c. Analyze working standards together with samples and blanks (steps 11 through 14).
   d. Prepare calibration graph of recovery vs. amount (µg) of formaldehyde added.
10. Analyze three quality control spikes and three analyst spikes to ensure that calibration and recovery graphs are in control.

MEASUREMENT:

11. Set liquid chromatograph according to manufacturer's recommendations and to conditions given on page 2016-1.
12. Transfer a 3-mL aliquot of the solution from step 7. to a 4-mL vial. Cap the vial.
13. Inject a 20-µL sample aliquot.
14. Measure peak area.
    NOTE 1: If peak area is greater than the highest standard, take a smaller aliquot of the remaining unreacted sample solution, dilute to 1 mL with acetonitrile , reanalyze, and apply appropriate dilution factor in the calculations.
    NOTE 2: To ensure validity of the samples, all samples containing over 6 to 7 µg/mL should be reported as a lower limit and the samples recollected at a lower total sample volume, since the maximum amount of formaldehyde that can react with 2,4-dinitrophenylhydrazine is 70 µg. In these instances, the capacity of the sampler may have been exceeded
    NOTE 3: The peak area for the DNPH peak should be at least 20 % of the formaldehyde-DNPH peak. If the DNPH peak area is less than this amount, then the capacity of the sampler may have been exceeded and the analytical results will be biased low. If this situation is observed the sample results may be reported as a lower limit and the workplace resampled using a smaller total sample volume.

CALCULATIONS:

19. Determine mass, µg, of formaldehyde, W, found in the sample and the average media blank, B, from the calibration graph.
    NOTE: Include dilution factor for any sample which exceeded the highest calibration standard.
20. Calculate concentration, C, of formaldehyde in the air volume sampled, V (L).

$$C = \frac{W - B}{V}, \text{ mg/m}^3$$

EVALUATION OF METHOD:

The evaluation of this method was based in part on data generated at NIOSH and Waters Corporation. Generated sample results were provided by Waters [1] and spiked sample results were obtained at NIOSH. This method was evaluated over the range of 0.5 to 55 µg/sample. Overall measurement precision, $\hat{S}_{rT}$, was 0.057 based on NIOSH guidelines [8] including a 5% pump error factor and estimated bias was +4.4%. Sample stability during storage was evaluated over the range of 0.5 to 55 µg formaldehyde/sample. Samples showed from 1 to 20% loss (dependent on loading) after storage for 7 days at ambient temperature and 4 to 7% loss when stored up to 14 days at 4° C, compared to one-day old samples. An additional study found that losses were 5% or less after 4 days' storage at ambient temperature.

Capacity of the sampler was found to vary with relative humidity (RH). When sampling a concentration of 2.5 mg/m^3 of formaldehyde, capacity of the sampler to collect formaldehyde at 85% RH was 95 µg and at 10% RH, 59 µg. Based on this information, a maximum capacity of 38 µg was calculated. The limit of quantitation of the method for formaldehyde was 0.6 µg per sampler. This corresponds to a concentration of 0.02 ppm in a 22.5 liter sample.

The method can be used for the measurement of both STEL and time weighted average exposure measurements. The estimated accuracy of the method is 19% with a 95% confidence interval of 16 to 22%. The upper 95% confidence limit on accuracy for the method is 22%, which meets the NIOSH accuracy criterion of ±25% [8].

REFERENCES:

[1] Iraneta PC, Collamati RA, Costello DN, Crowley RJ, Fernandes RL, Hopkins MR, Knowles CE, Martin DM. A validation study of a new active sampler for the analysis of formaldehyde in workplace and indoor air. Am Ind Hyg Assoc J: In press.

[2] NIOSH [1994]. Formaldehyde: Method 5700. In: Eller PM, Cassinelli ME, Eds. NIOSH Manual of Analytical Methods (NMAM), 4th ed. Cincinnati, OH: National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 94-113.

[3] Lipari F, Swarin S [1982]. Determination of formaldehyde and other aldehydes in automobile exhaust with an improved 2,4-dinitrophenylhydrazine method. J Chromatography *247*:297-306.

[4] OSHA [1985]. Method 52. OSHA Analytical Methods Manual. Salt Lake City, UT: U. S. Department of Labor, Occupational Safety and Health Administration, OSHA Analytical Laboratory.

[5] NIOSH [1994]. Formaldehyde: Method 3500. In:Eller PM, Cassinelli ME, Ed. NIOSH Manual of Analytical Methods (NMAM),4th ed. Cincinnati, OH: National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 94-113.

[6] NIOSH [1994]. Formaldehyde: Method 2541. In: Eller PM, Cassinelli ME, Eds. NIOSH Manual of Analytical Methods (NMAM),4th ed. Cincinnati, OH: National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 94-113.

[7] Waters Corporation [1994]. Waters Sep-Pak XPoSure Aldehyde Sampler Care and Use Manual. Milford, MA: Waters Corporation:p. 31.

[8] Kennedy ER, Fischbach TJ, Song R, Eller PE, Shulman SA [1995]. Guidelines for air sampling and analytical method development and evaluation. Cincinnati, OH: National Institute for

Occupational Safety and Health, DHHS (NIOSH) Publication No. 95-117.

[9] NIOSH/OSHA [1981]. Occupational health guidelines for occupational hazards. U. S. Department of Health and Human Services, National Institute for Occupational Safety and Health ,DHHS (NIOSH) Publication No. 81-123. Available as GPO Stock #017-033-00337-8 from Superintendent of Documents, Washington, D. C. 20402.

METHOD WRITTEN BY:

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APPENDIX:

PREPARATION AND STANDARDIZATION OF FORMALDEHYDE STOCK SOLUTION (ca. 1 mg/mL)

Dilute 2.7 mL 37% aqueous formalin solution to 1 L with distilled, deionized water. This solution is stable for at least three months. Standardize by placing 5.0 mL of freshly prepared 1.1*N* sodium sulfite solution in a 50-mL beaker and stir magnetically. Adjust pH to between 8.5 and 10 with base or acid. Record the pH. Add 10.0 mL formaldehyde stock solution. The pH should now be greater than 11. Titrate the solution back to its original pH with 0.02*N* sulfuric acid (1 mL acid = 0.600 mg formaldehyde; about 17 mL acid needed). If the endpoint pH is overrun, back-titrate to the endpoint with 0.01*N* sodium hydroxide. Calculate the concentration, Ç (mg/mL), of the formaldehyde stock solution:

$$C_s = \frac{30.0\ (N_a\ V_a - N_b\ V_b)}{V_s}$$

where: 30.0 = 30.0 g/equivalent of formaldehyde
N_a = normality of sulfuric acid (0.02N)
V_a = volume of sulfuric acid (mL) used for titration
N_b = normality of NaOH (0.01N)
V_b = volume of NaOH (mL) used for back-titration
V_s = volume of formaldehyde stock solution (10.0 mL)